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## PROTON NMR STUDIES OF ROOM TEMPERATURE MOLTEN SALTS

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PROJECT 2303

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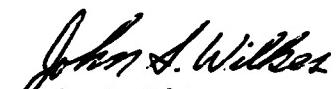
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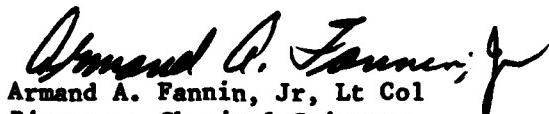
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**PROTON NMR STUDIES OF ROOM TEMPERATURE MOLTEN SALTS**

By

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JUNE 1982

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**Directorate of Chemical Sciences  
The Frank J. Seiler Research Laboratory  
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20. The model implies that the melts are relatively organized in the liquid state, especially basic compositions. The addition of LiCl or non-electrolyte solvents to binary aluminum chloride-imidazolium or -pyridinium chloride mixtures also affects chemical shifts of the cation protons.

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## SUMMARY

Mixtures of 1-(1-butyl)pyridinium chloride or 1-methyl-3-ethyimidazolium chloride with aluminum chloride are liquid at room temperature. The chemical shifts of protons on the cations of the melts are highly dependent on the proportions of aluminum chloride and organic chloride salt. The largest effect is in the basic melts, where there is an excess of organic chloride over aluminum chloride. The chemical shift behavior may be explained by assuming that the anions in the melt affect the chemical shift of the cation hydrogens and that the anions and cations interact in the fast exchange regime on the NMR time scale. The model implies that the melts are relatively organized in the liquid state, especially basic compositions. The addition of LiCl or non-electrolyte solvents to binary aluminum chloride-imidazolium or -pyridinium chloride mixtures also affects chemical shifts of the cation protons.

## PREFACE

The data reported here are part of a larger study that includes the measurement of  $^{13}\text{C}$  and  $^{27}\text{Al}$  NMR spectra of room temperature chloroaluminate molten salts. The purpose of the research is to understand the anion-cation interactions in the molten salts and correlate them to transport and other physical properties. Part of the work was done as USAF Reserve projects by Major Levisky and Captain Hussey. We acknowledge the valuable suggestions of Drs. Larry Dalton and W. Robert Carper.

## INTRODUCTION

Fused salts that are liquid at room temperature comprise an unconventional but interesting class of aprotic solvents for studying the chemistry of inorganic, organometallic, and organic solutes. In addition, these ionic liquids are potentially useful as electrolytes in batteries, photoelectrochemical cells, and electroplating. In recent years some mixtures of aluminum chloride and 1-alkylpyridinium halides (1,2) or 1,3-dialkylimidazolium chlorides (3) have been shown to be liquid below room temperature. An understanding of the physical and chemical properties of the melts is vital to establishing the usefulness of the new materials. Especially important are the transport properties, such as electric conductivity and viscosity. In turn these physical properties are dependent on the detailed structure of the molten salt. In order to understand better the melt structure, we have studied the interactions between the anions and cations in the melts by nuclear magnetic resonance (NMR) spectroscopy.

Proton NMR is an established technique for studying  $\pi$ -complexes (4) and hydrogen bonded systems (5). Since the chloroaluminate melts mentioned above have cations with protons that are readily observable by NMR, we have attempted to deduce some aspects of the structure of the low melting salts from NMR experiments. We have chosen one example from each of the two types of chloroaluminate melts mentioned above; 1-methyl-3-ethylimidazolium ( $\text{MeEtIm}$ ) and 1-(1-butyl)pyridinium ( $\text{BuPy}$ ) chloride.

## EXPERIMENTAL

**Apparatus.** Nuclear magnetic resonance spectra were recorded at 60 MHz on a Varian T-60A or a Hitachi Perkin-Elmer R-24P spectrometer.

**Reagents.** Chloroaluminate melts were prepared from purified  $\text{AlCl}_3$  and 1-(1-butyl)pyridinium chloride (6) or 1-methyl-3-ethylimidazolium chloride (3) as described elsewhere.

**Procedure.** The NMR spectra were obtained from samples contained in 5mm tubes, which were loaded in dry argon or nitrogen atmosphere glove boxes. Either an internal standard of chlorotrimethylsilane or an external standard of DMSO was added and the tubes were securely capped to exclude moisture. The temperature was maintained constant during the NMR measurements ( $35 \pm 1^\circ\text{C}$  for pyridinium melts and  $34 \pm 1^\circ\text{C}$  for the imidazolium melts)

## **RESULTS**

The proton NMR spectra and assignments of 1-methyl-3-ethylimidazolium chloride in  $d_6$ -DMSO are shown in figure 1. The protons were assigned according to similar imidazolium iodides reported by others (7). The spectrum of 1-alkylpyridinium chloride and its assignments have been published (8). Fortunately, most of the resonances are well separated. The spectra of chloroaluminate melts (i.e. mixtures with  $\text{AlCl}_3$ ) prepared from MeEtIm chloride or BuPy chloride are very similar to the spectra of the chlorides in solution. Examples of the spectra of melts are shown in figures 2 and 3. These spectra are of the neat liquids at slightly above room temperature, and are very similar to the dissolved chloride salts. The signal to noise ratio is excellent and the resolution of the multiplets is only slightly degraded from the solution spectra, probably due to the higher viscosity of the melts.

The dependence of proton chemical shifts on  $\text{AlCl}_3$  mole fraction in the melts is most interesting. Figures 4 and 5 show the changes in shifts for the MeEtIm and BuPy chloroaluminate melts respectively for all of the ring protons and most of the protons on the alkyl substituents. The resonances for some of the protons on the butyl group of the BuPy cation are not plotted, because they did not change significantly and could not be resolved very well. In both types of melts the ring protons located on carbons adjacent to nitrogen were most affected by changes in  $\text{AlCl}_3$  mole fraction. Two things are immediately evident; there is a sharp change in behavior at 0.5 mole fraction

$\text{AlCl}_3$ , and chemical shifts in basic melts (mole fraction  $\text{AlCl}_3 < 0.5$ ) are more sensitive to composition changes than for acidic melts (mole fraction  $\text{AlCl}_3 > 0.5$ ). The effect of size of the alkyl substituents on the chemical shifts is demonstrated in 1,3-dialkylimidazolium chloride -  $\text{AlCl}_3$  melts in figure 6.

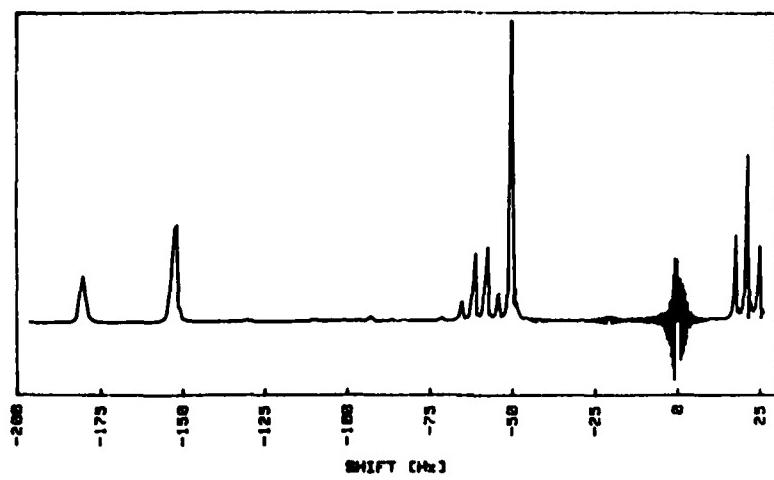
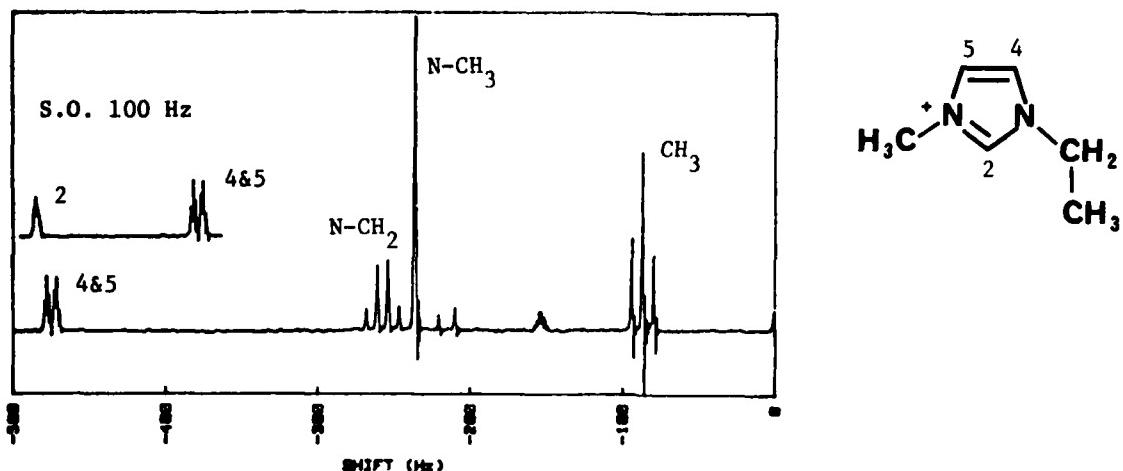


Figure 2. Proton NMR spectrum of neat 1-methyl-3-ethylimidazolium chloride - aluminum chloride melt. Mole fraction  $\text{AlCl}_3$  is 0.667. Reference is DMSO.

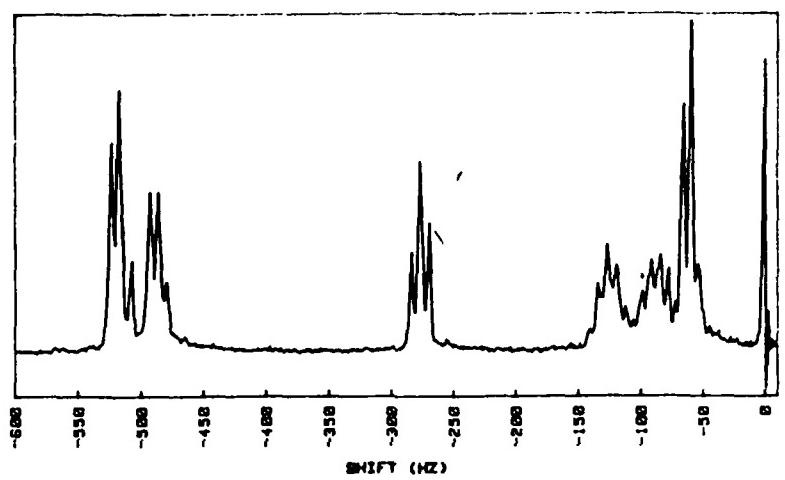


Figure 3. Proton NMR spectrum of neat 1-butylpyridinium chloride - aluminum chloride melt. Mole fraction  $\text{AlCl}_3$  is 0.52. Reference is chlorotrimethylsilane.

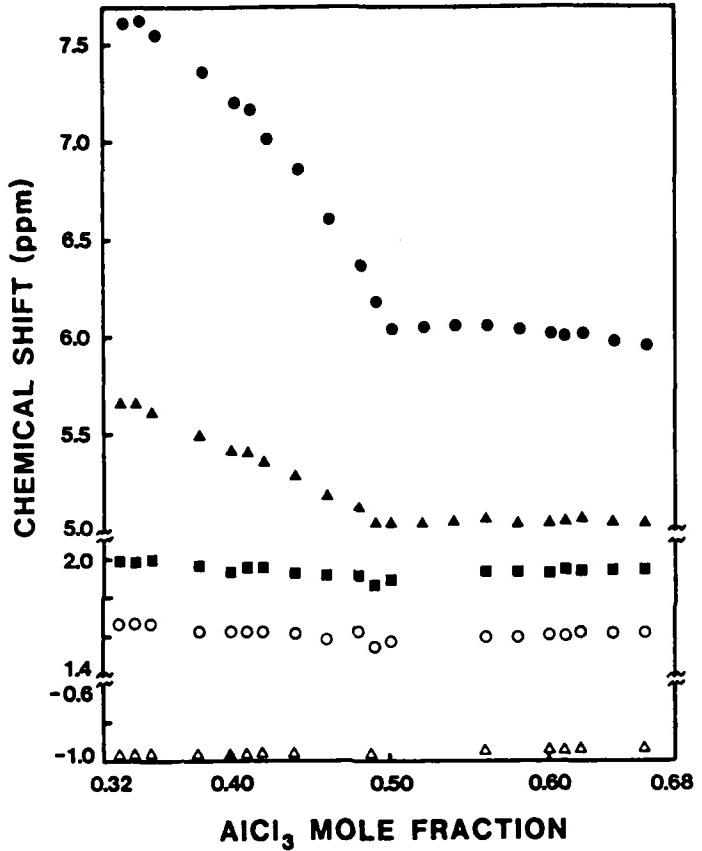


Figure 4. Proton chemical shifts in neat 1-methyl-3-ethylimidazolium chloride - aluminum chloride melts versus mole fraction  $\text{AlCl}_3$ . (●) H-2 proton, (▲) H-4&5 protons (average of unresolved multiplet), (■) N- $\text{CH}_2$  protons, (○) N- $\text{CH}_3$  proton, ( $\Delta$ )  $\text{CH}_3$  proton. Reference is DMSO external standard.

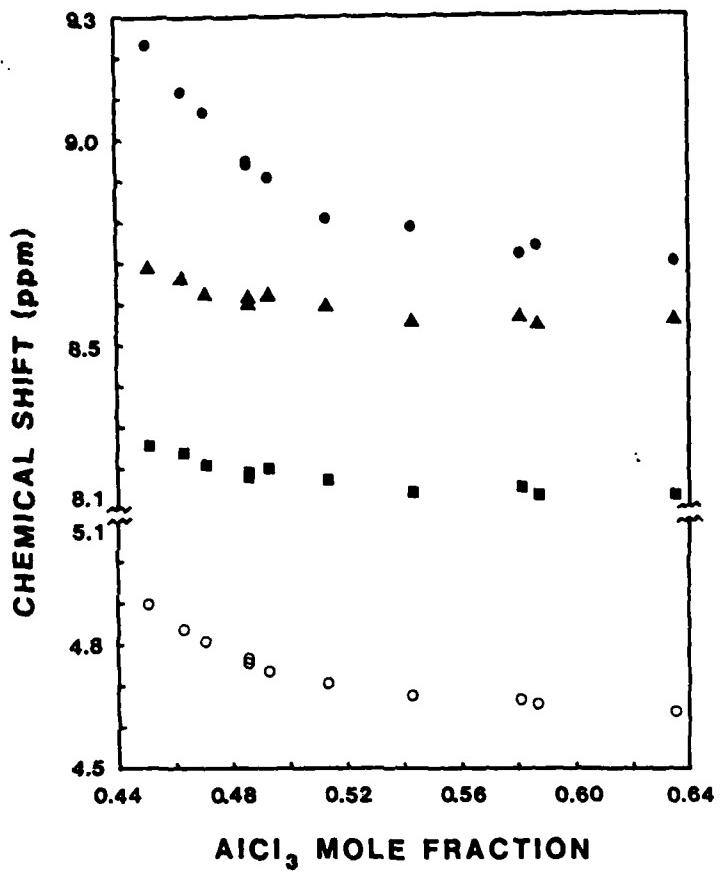


Figure 5. Proton chemical shifts in neat 1-butylpyridinium chloride - aluminum chloride melts versus mole fraction AlCl<sub>3</sub>. (●) 2,6 protons, (▲) 3,5 protons, (■) 4 proton, (○) N-CH<sub>2</sub> proton. Reference is chlorotrimethylsilane internal standard.

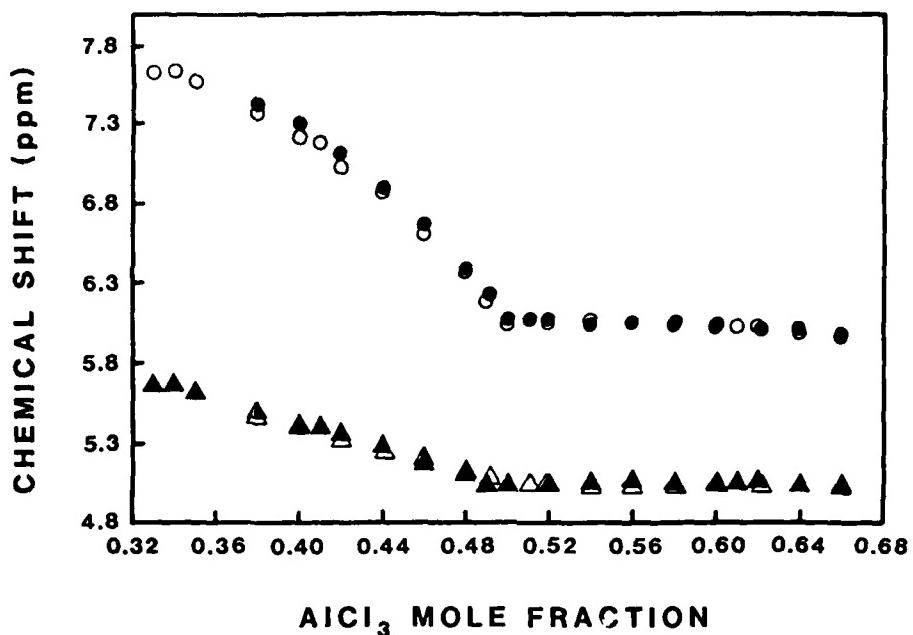
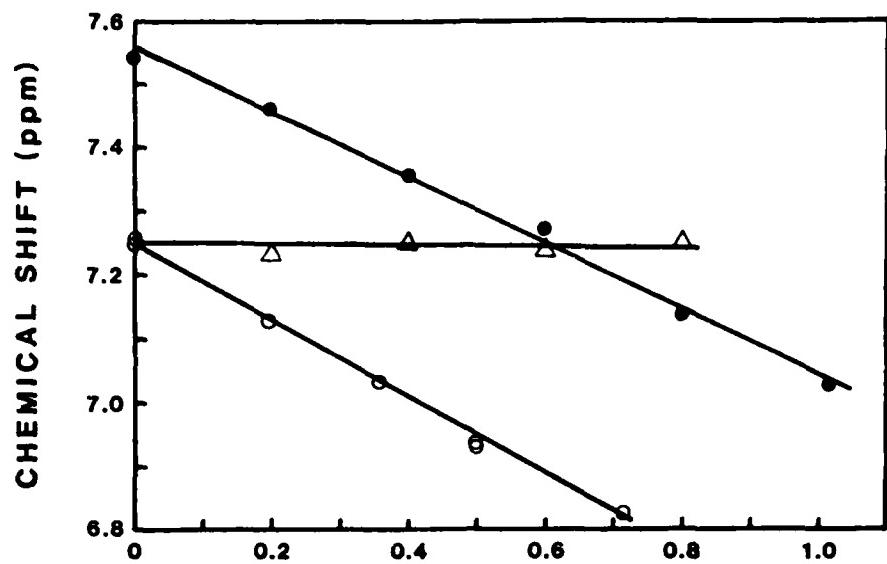


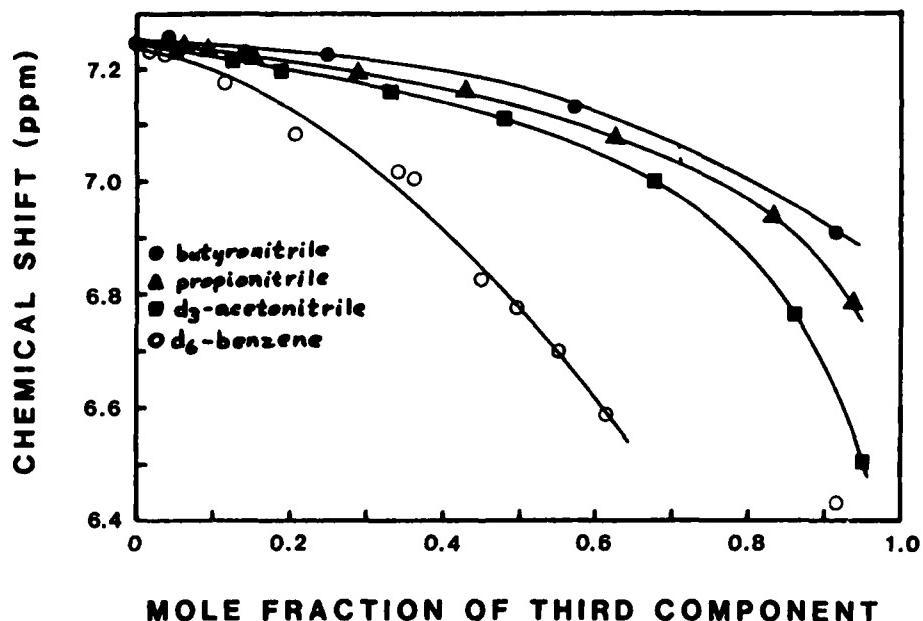
Figure 6. Proton chemical shifts in neat 1-methyl-3-ethylimidazolium chloride - aluminum chloride melts (open symbols) and 1-methyl-3-butylimidazolium chloride - aluminum chloride melts (filled symbols) versus mole fraction  $\text{AlCl}_3$ . ( $\circ$  &  $\square$ ) H-2 proton, ( $\Delta$  &  $\blacktriangle$ ) H-4&5 protons (average of unresolved multiplet)

The addition of a third component to binary MeEtIm chloroaluminate melts may also affect chemical shifts of protons on the cation. The effects of LiCl and BuPyCl added to melts at constant  $\text{AlCl}_3$  mole fraction is shown in figure 7. The effects of several non-electrolytes on the binary MeEtIm melt is shown in figure 8. In the cases shown in figure 8 the addition of a third component results in upfield changes in chemical shifts.



#### MOLE FRACTION OF THIRD COMPONENT

Figure 7. Proton chemical shifts of H-2 proton in neat ternary melts. (△) AlCl<sub>3</sub>/MeEtImCl/BuPyCl, AlCl<sub>3</sub> mole fraction = 0.40; (○) AlCl<sub>3</sub>/MeEtImCl/LiCl, AlCl<sub>3</sub> mole fraction = 0.40; (●) AlCl<sub>3</sub>/MeEtImCl/LiCl, AlCl<sub>3</sub> mole fraction = 0.35.



#### MOLE FRACTION OF THIRD COMPONENT

Figure 8. Proton chemical shifts of H-2 proton in neat 1-methyl-3-ethylimidazolium chloride - aluminum chloride - solvent melts versus mole fraction solvent. (●) butyronitrile, (△) propionitrile, (■) d<sub>3</sub>-acetonitrile, (○) d<sub>6</sub>-benzene.

## DISCUSSION

Some clues to the interpretation of the changes in shifts with changing proportion of  $\text{AlCl}_3$  may be found in work done on some similar molten salts. Newman et al. have recently reported that for some pyridinium and picolinium halides the chemical shifts of the N-H protons are more deshielded (shifted downfield to higher  $\delta$  values) in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$  (9). This is in accordance with the relative hydrogen-bonding abilities of those halides, and is evidence that the pyridinium chlorides and bromides exist as hydrogen-bonded complexes. The ring protons in the same melts exhibit the reverse order for deshielding by the halides, implying that simple electrostatic interactions do not occur between the anion and cation. The direction of change of the shift is in precisely the opposite direction in our experiments, where the  $\text{Cl}^-$  is being smoothly replaced by  $\text{AlCl}_4^-$  in the basic melts. The ring protons in both the 1-methyl-3-ethylimidazolium and 1-(1-butyl)pyridinium cations shift upfield as the  $\text{Cl}^-$  is replaced with  $\text{AlCl}_4^-$ , which should be a weaker inducer of negative charge.

Angell and Shuppert (10) have studied the proton NMR behavior of some pyridinium melts that are more closely related to ours. These workers added  $\text{AlCl}_3$  or  $\text{ZnCl}_2$  to pyridinium chloride, and observed changes in both N-H and ring protons. The N-H shifts moved upfield as  $\text{AlCl}_4^-$  replaced  $\text{Cl}^-$  upon addition of  $\text{AlCl}_3$ , as expected according to the results of Newman. The ring proton resonances on the pyridinium cations moved upfield with increasing  $\text{AlCl}_3$  up to about 0.25 mole fraction  $\text{AlCl}_3$ , then moved downfield for some protons and continued upfield for others above 0.25 mole fraction  $\text{AlCl}_3$ .

The explanations provided by Angell and by Newman for their data are not strictly applicable to our melts, since the existence of hydrogen-bonding clearly has a profound effect on chemical shifts. Osteryoung and coworkers (8) have done  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments on melts very similar (and in one

case identical) to those we report here. While Osteryoung and coworkers did not study a large number of compositions, they did examine melts where bromine was substituted for chlorine (ie. EtPyBr-AlCl<sub>3</sub> and EtPyBr-AlBr<sub>3</sub>). From the lack of differences in ring proton chemical shifts for the chlorine and bromine containing melts, they concluded that there was no pyridinium-halide ion pairing in acidic melts. This is in accord with our observations (figures 4 and 5), where we saw only small changes in chemical shifts in acidic melts. In the acidic melts, we presume that all halide atoms are in the form AlCl<sub>4</sub><sup>-</sup> or Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>. A major difference between our work and Osteryoung's is that we have concentrated our efforts on basic melts, where the Cl<sup>-</sup> activity is high, rather than acidic melts, where Cl<sup>-</sup> activity is very low.

In general terms it appears that the less polarizable the anions are, the greater the effect on proton chemical shifts. The organic chloride salt - aluminum chloride melts that we have studied are in some ways simpler than Newman's or Angell's systems in terms of anion-cation interactions, since no hydrogen-bonding is possible. They are more complex in the sense that three different anions need to be considered (Cl<sup>-</sup>, AlCl<sub>4</sub><sup>-</sup>, and Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>), although never more than two will be present in significant quantities at any given composition, because of the very low value of the equilibrium constant for  $2\text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^- + \text{Cl}^-$ . The observed direction of chemical shift changes agrees with the qualitative expectation that as greater negative charge is induced into the imidazolium cation (by Cl<sup>-</sup> relative to AlCl<sub>4</sub><sup>-</sup>) the ring anisotropy is increased and the ring protons are more shielded.

In order to quantitatively interpret the changes in chemical shifts with composition, we have made some assumptions about the anion-cation interactions and how they affect chemical shift. The fundamental assumptions about the

interactions are that they exist, that they can affect shifts by modifying the net charge of the cation, and that the "complexes" formed are relatively weak so that fast exchange (on the NMR time scale) occurs. The term "complex" means here an identifiable (but probably not isolable) species whose structure may be formulated reasonably from the melt composition, but is probably weaker than charge transfer or hydrogen-bonded complexes.

If the system is in the fast exchange regime, the chemical shifts of protons of the cations is the population weighted average of the chemical shifts of the different complexes present, as expressed by equation 1, where  $\delta_i$  and  $X_i$  are the chemical shifts and mole fractions of the complexes.

$$\delta_{\text{obs}} = \sum_{i=1}^n \delta_i X_i \quad (1)$$

In order to simplify the discussion we will consider only the MeEtIm melts from here on, but the same results were obtained for the BuPy melts as well.

The simplest model (Model 1) for the melt is where the ions exist as simple ion pairs, that is, each cation is coordinated with a single anion and vice versa. In order to determine which pairs should be present at a given melt composition and what their mole fractions are, it is instructive to calculate the fractions of the various anions as a function of composition (figure 9) for the composition range  $0 < X_{\text{AlCl}_3} < 0.67$ . At  $\text{AlCl}_3$  mole fraction of 0, 0.5 and 0.67 only a single anion is present:  $\text{Cl}^-$ ,  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  respectively. In basic melts varying proportions of  $\text{Cl}^-$  and  $\text{AlCl}_4^-$  are present and in acidic melts varying proportions of  $\text{Al}_2\text{Cl}_7^-$  and  $\text{AlCl}_4^-$  exist. For ion pairs there are three possible complexes, but a maximum of two will exist in any significant quantities at any given composition. (The notation for the complexes indicates the total number of chlorine atoms associated with the cation.)

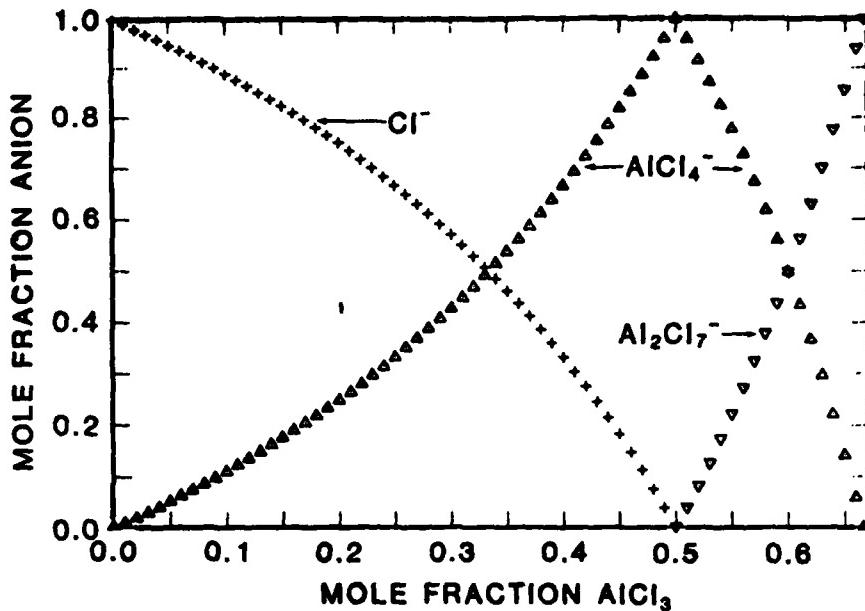
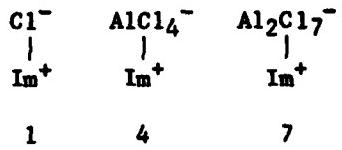


Figure 9. Calculated anion fractions versus mole fraction  $\text{AlCl}_3$  in chloroaluminate melts.

Equation 1 becomes

$$\delta_{\text{obs}} = \delta_1 X_1 + \delta_4 X_4 + \delta_7 X_7 \quad (2)$$

The observed shifts as a function of the  $X_i$ 's may be fitted to equation 2, because each  $X_i$  for each species is equal to the anion mole fraction of the anion the species contains, and the anion fractions ( $Y_i$ ) may be calculated from the mole fraction  $\text{AlCl}_3$  ( $X_{\text{AlCl}_3}$ ) as follows:

basic compositions:  $Y_{\text{Cl}^-} = \frac{1 - 2X_{\text{AlCl}_3}}{1 - X_{\text{AlCl}_3}} = X_1$

$$Y_{\text{AlCl}_4^-} = \frac{X_{\text{AlCl}_3}}{\frac{1 - X_{\text{AlCl}_3}}{12}} = X_4$$

$$\text{acidic compositions: } Y_{\text{AlCl}_4^-} = \frac{2 - 3X_{\text{AlCl}_3}}{1 - X_{\text{AlCl}_3}} = X_a$$

$$Y_{\text{Al}_2\text{Cl}_7^-} = \frac{2X_{\text{AlCl}_3} - 1}{1 - X_{\text{AlCl}_3}} = X_b$$

The models were tested for only the basic compositions, since acidic compositions show little change in shifts with  $\text{AlCl}_3$  mole fraction. Since  $\delta_a$  is  $\delta_{\text{obs}}$  at 0.5 mole fraction  $\text{AlCl}_3$ , the experimental value was used rather than a fitted value. The shifts calculated for MeEtIm melts according to equation 2 are plotted as dashed lines in figure 10 along with the observed data. The calculated lines agree reasonably well for all of the protons except the H-2 proton (the proton attached to carbon number 2). However, since not all of the data could be fitted with equation 2, one of the assumptions probably is incorrect.

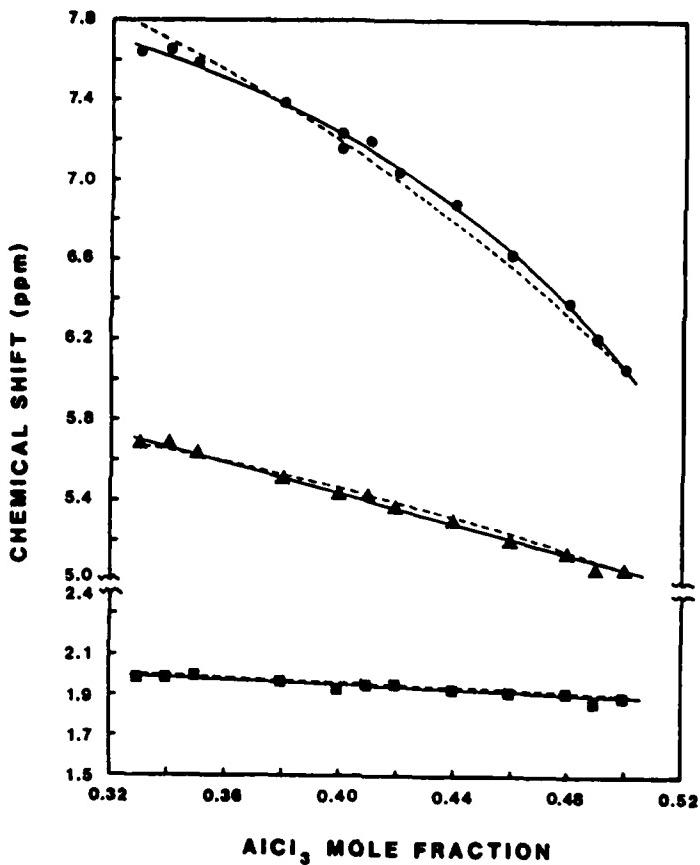
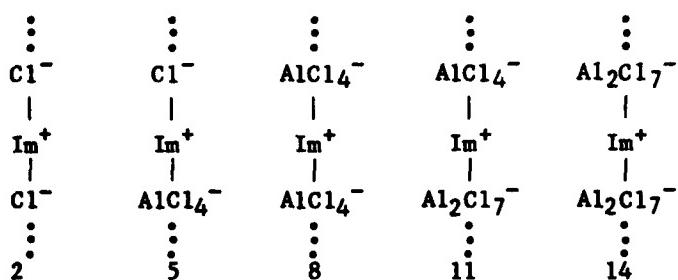


Figure 10. Proton chemical shifts in neat 1-methyl-3-ethyimidazolium chloride - aluminum chloride melts versus mole fraction  $\text{AlCl}_3$ . (●) H-2 proton, (▲) H-4&5 protons (average of unresolved multiplet), (■) N- $\text{CH}_2$  protons, (-----) predicted from equation 2, (—) predicted from equation 3.

That the anions and cations exist as ion pairs (coordination number = 1) is the weakest of the assumptions. It would be more reasonable to assume that each cation may interact with two or more anions, and vice versa. For coordination number of two, an analysis similar to the one above for ion pairs may be made. In this case (Model 2) five different complexes are possible, as shown below:



Species 1 through 5 are not discrete, but represent portions of oligomeric chains of alternating cations and anions. For Model 2 equation 1 becomes

$$\delta_{\text{obs}} = \delta_2 X_2 + \delta_5 X_5 + \delta_8 X_8 + \delta_{11} X_{11} + \delta_{14} X_{14} \quad (3)$$

If the distribution of the five complexes is determined by a random distribution of the anions among the cations, then the  $X_i$ 's may be calculated from the anion mole fractions, similar to the way they were calculated for Model 1. Thus the  $X_i$ 's for equation 3 are:

$$\text{basic compositions: } X_2 = Y_{\text{Cl}^-}^2$$

$$X_5 = 2 \cdot Y_{\text{Cl}^-} \cdot Y_{\text{AlCl}_4^-}$$

$$\text{all compositions: } X_8 = Y_{\text{AlCl}_4^-}^2$$

$$\text{acidic compositions: } X_{11} = 2 \cdot Y_{\text{AlCl}_4^-} \cdot Y_{\text{Al}_2\text{Cl}_7^-}$$

$$X_{14} = Y_{\text{Al}_2\text{Cl}_7^-}^2$$

The values of  $\delta_2$ ,  $\delta_5$  and  $\delta_{14}$  are the observed chemical shifts at  $\text{AlCl}_3$  mole fractions 0, 0.5 and 0.67. No measurement was made at 0 mole fraction  $\text{AlCl}_3$ , since that composition is not a liquid at room temperature. The experimental value for  $\delta_5$  was used in equation 3 and the remaining  $\delta_i$ 's were obtained by curve fitting. The calculated shifts for the MeEtIm chloroaluminate melts are shown as solid lines in figure 10. In contrast to the earlier model, this one fits all of the experimental data very well.

The model where the coordination number of each ion was three (Model 3) was tested by a procedure entirely analogous to that for the Model 2 discussed

above. The model involves seven possible complexes, and five of the  $\delta_i$ 's are fittable parameters. With that many fittable parameters almost any curve could be matched by the fit. In the case of the three coordinate model the fit was only negligibly better than the two coordinate model.

The assumption that the anions are randomly distributed among the cations could be false. One could envision that the anions are distributed such that there are chloride-rich, tetrachloroaluminate-rich and heptachloroaluminate rich regions, where complexes 2, 8 and 14 are preferred (Model 2A). Alternatively, complexes 2, 8 and 14 may be selectively avoided, resulting in a melt structure that maximizes cations associated with different anions (Model 2B). The complexes present would be the same as those presented earlier for Model 2, but their mole fractions would be different. In order to test Models 2A and 2B we calculated the shifts according to equation 3 using  $X_i$ 's appropriate to the limiting non-random distributions. The mole fractions of the complexes for Model 2A and 2B in the basic melts become:

Model 2A:

$$X_2 = \frac{X_{AlCl_3}}{1 - X_{AlCl_3}}$$

$$X_8 = 0$$

$$X_{14} = \frac{1 - 2X_{AlCl_3}}{1 - X_{AlCl_3}}$$

Model 2B:

$$X_2 = 0$$

$$X_8 = \frac{2 - 4X_{AlCl_3}}{1 - X_{AlCl_3}}$$

$$X_{14} = \frac{3X_{AlCl_3} - 1}{1 - X_{AlCl_3}}$$

These expressions of the  $X_i$ 's were used in equation 3 to predict chemical shift changes, and substantially poorer fits were obtained compared with the random distribution model (Model 2).

The quality of the fits for the models having different assumptions and coordination numbers is summarized in table 1.

Table 1  
Comparison of Fits to Chemical Shift Data

| model     | Standard Deviation for Fits of Proton Chemical Shifts (ppm) |                  |                              |
|-----------|---|------------------|------------------------------|
|           | H-2<br>protons  | H-4&5<br>protons | N-CH <sub>2</sub><br>protons |
| Model 1   | 0.0529  | 0.0185           | 0.0144                       |
| Model 2   | 0.0197  | 0.0140           | 0.0143                       |
| Model 2A  | 0.0529  | 0.0185           |                              |
| Model 2B  | 0.0494  | 0.0188           | 0.0144                       |
| Model 3   | 0.0195  | 0.0140           |                              |
| Quadratic | 0.0203  |                  |                              |

The values of  $\delta_i$ 's from Model 2 are:  $\delta_2 = 8.25$  ppm,  $\delta_5 = 8.14$ ,  $\delta_6 = 6.05$ ,  $\delta_{11} = 6.07$  and  $\delta_{11} = 5.97$ .

The size of the alkyl substituents in the dialkylimidazolium cations has a substantial effect on transport properties (11). However, the anion-cation interactions are hardly affected at all, as seen in figure 6. The dependence of proton chemical shifts of the H-2 and H-4&5 protons in 1-methyl-3-butylimidazolium chloride - AlCl<sub>3</sub> melts is the same as for the MeEtImCl-AlCl<sub>3</sub> melts discussed above.

It is clear that the chemical shift behavior of these cations in chloroaluminate melts may be explained in terms of the interactions of the anions and cations using a simple model. It follows that anything that is added to the melt that could change the anion-cation interactions would also change the proton NMR chemical shifts. Alkali metal chlorides and organic solvents are two types of materials that could affect the anion-cation complexes.

Lithium chloride is soluble in basic MeEtIm chloroaluminate melts up to

approximately 0.1 mole fraction LiCl. NaCl, KCl, RbCl and CsCl are not sufficiently soluble to study their effect on chemical shifts. Since the chloride mole fraction in the melt has a great effect on the chemical shifts of the cation protons, the experiments with added LiCl were performed at constant AlCl<sub>3</sub> mole fraction. This insures that the anion fractions remain constant. The experiments may be viewed as a replacement of the imidazolium chloride with lithium chloride. Figure 7 shows that there is an almost linear decrease in the chemical shift of the H-2 proton with increasing LiCl mole fraction. The behavior may be rationalized qualitatively by viewing Li<sup>+</sup> as a better competitor for negative charge from the anions than are the imidazolium cations. As the LiCl fraction increases, the fraction of Im<sup>+</sup> ions whose nearest cation neighbor is Li<sup>+</sup> increases, resulting in a higher proportion of Im<sup>+</sup> containing complexes that have a diminished induction of negative charge. We have not yet developed a quantitative model that satisfactorily explains the LiCl ternary data.

Ternary mixtures composed of MeEtImCl, AlCl<sub>3</sub> and an organic non-electrolyte also show interesting changes in proton chemical shifts of the Im<sup>+</sup> cation (figure 8). In the four non-electrolytes studied the shifts move upfield with increasing mole fraction of non-electrolyte. Again, we can interpret the changes in terms of the modification of the anion-cation interactions. We propose that the effect of added solvent at the molecular level is to break up the ionic interactions, thus reducing the electrostatic influence of the anion on the cation. Greater amounts of solvent would show a greater effect. Three of the solvents studied are a homologous series of nitriles; acetonitrile, propionitrile and butyronitrile. Acetonitrile has the greatest effect, propionitrile a lesser effect, and butyronitrile the least. That order is the same as the order of dielectric constants for the solvents, and one would expect that the greater the dielectric constant the more effec-

tive the solvent would be in solvating the ions.

Benzene presents an especially interesting case. Because it is quite non-polar, it is somewhat surprising that benzene is soluble at all in the totally ionic melts, although Osteryoung and coworkers have reported that it was soluble in the BuPy chloroaluminates, it modified the electric conductivity and it affected proton and carbon chemical shifts of the cation (8). It is not as soluble in the basic melts as the series of nitriles (which are miscible in all proportions), but it has a greater effect on the chemical shifts of the cation protons in the range where it is soluble. This may be due to a more specific interaction between the imidazolium cation and benzene, such as the complex between the two aromatic species suggested for the BuPy melts (8). In any case the effect is the same as for the nitriles, i.e. the anions have less influence on the cations and the chemical shifts are moved upfield.

The chemical shift change of the H-2 proton is a sensitive indicator of composition for basic melts, and may be used as an analytical method for composition determinations. Fortunately the data may be fitted relatively well to a quadratic (equation 4), as demonstrated in table 1. The fit is only

$$\delta_{\text{obs}} = a(X_{\text{AlCl}_3})^2 + bX_{\text{AlCl}_3} + c \quad (4)$$

slightly poorer than the fit to equation 3, and still within experimental error. The expression for X is then obtained from the quadratic formula, which is equation 5.

$$X_{\text{AlCl}_3} = \frac{-b - \sqrt{b^2 - 4a(c - \delta_{\text{obs}})}}{2a} \quad (5)$$

The a, b and c parameters for equation 5 are tabulated in table 2.

Table 2  
Quadratic Fit Parameters.

| organic chloride             | a      | b      | c     | Temperature (°C) |
|------------------------------|--------|--------|-------|------------------|
| 1-(1-butyl)pyridinium        | 47.51  | -52.79 | 23.39 | 35 ± 1           |
| 1-methyl-3-ethyylimidazolium | -34.24 | 19.06  | 5.07  | 34 ± 1           |

#### CONCLUSIONS

Proton NMR chemical shifts of the hydrogens located in the cations of organic chloride - aluminum chloride room temperature molten salts are sensitive to the composition of melts. The changes in chemical shifts may be explained by a model that distributes the imidazolium cation among five different anion-cation complexes. Addition of lithium chloride or one of several organic solvents disrupts the complexes and changes the proton chemical shifts.

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ABBREVIATIONS AND ACRONYMS

|                      |                             |
|----------------------|-----------------------------|
| NMR                  | nuclear magnetic resonance  |
| MeEtIm               | 1-methyl-3-ethylimidazolium |
| BuPy                 | 1-(1-butyl)pyridinium       |
| DMSO                 | dimethylsulfoxide           |
| d <sub>6</sub> -DMSO | deuterated DMSO             |
| δ                    | chemical shift              |
| X                    | mole fraction               |
| Im <sup>+</sup>      | imidazolium                 |
| Y                    | anion fraction              |
| d                    | deuterium substitution      |
| TMS                  | tetramethylsilane           |